Zhu et al. Reply

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Zhu *et al.* Reply: In the preceding Comment [1], Gekle and Arnold raised two issues regarding our Letter [2]. (i) They claimed that we incorrectly derived a linear response equation for $\epsilon_\perp$ and (ii) our development invalidates our central result. This Reply aims to respond to both these points. First, Gekle and Arnold claimed that we incorrectly derive a linear response equation for $\epsilon_\perp$. In their demonstration, Gekle and Arnold [1] do not show this incorrectness. As mentioned in Refs. [2,3], we derived the Cartesian components of the dielectric permittivity, i.e., ϵ_{xx}, ϵ_{yy}, and ϵ_{zz} and not the radial component in cylindrical coordinates. Let us remind the reader that a cylindrical tensor can be transformed in a nondiagonal Cartesian tensor depending on r from a change of base. Therefore, we can define a Cartesian dielectric tensor. We show that the values of the nondiagonal elements are close to 0.0 and that $\epsilon_{xx} \sim \epsilon_{yy}$, leading to a Cartesian quasidiagonal tensor. However, by taking back our previous development and without alteration of our theoretical background, we provide, below, an explicit radial component in cylindrical coordinates, although in our approach this is useless. The inverse dielectric function can be written as $\Delta\mathbf{E}(r) = \epsilon_0^{-1}\epsilon^{-1}(r)\Delta\mathbf{D}$, where $\mathbf{E}$ is the electric field, r the norm of the radial vector, ϵ_0 the vacuum permittivity, and $\mathbf{D}$ the displacement field. In the radial direction, $\mathbf{D}(r)$ is uniform, and then $\nabla\mathbf{D}(r) = 0 \rightarrow (1/r)(\partial[rD_r(r)]/\partial r) = 0$. From integration, we obtain $D_r(r) = (D_\perp/r)$ that corresponds to the second term of Eq. (1) of Ref. [1]. As $\Delta\mathbf{D}(r) = \epsilon_0\Delta\mathbf{E} + \Delta\mathbf{m}(r)$, where $\Delta\mathbf{m}$ is the excess of dipolar polarization, we can write

$$\frac{\epsilon_\perp(r)(r) - 1}{\epsilon_\perp(r)(r)} = r\frac{\Delta\mathbf{m}_\perp(r)}{D_\perp}. \quad (1)$$

By using the relation of fluctuation dissipation to express $\Delta\mathbf{m}_\perp$ [2,3], we obtain

$$\frac{\epsilon_\perp(r) - 1}{\epsilon_\perp(r)} = r\frac{\langle m_\perp(r)M_\perp\rangle - \langle m_\perp(r)\rangle\langle M_\perp\rangle}{\epsilon_0 V_p(r)k_B T}. \quad (2)$$

Variables are defined in Ref. [2]. This relation corresponds to Eq. (8) of Ref. [1]. Thus, the theoretical framework behind $\epsilon_\perp$ is shown to be correct. However, we prefer to extract the Cartesian components of dielectric permittivity, given the independence of the symmetry and shape of the system.

Second, Gekle and Arnold claimed that our central result is invalidated, i.e., an unexpected increase in $\epsilon_\perp$ of NaCl solutions [2]. However, Gekle and Arnold have not demonstrated the absence of an increase in $\epsilon_\perp$ at low salt concentration. To definitively ensure our result and the underlying physics phenomena, we provide in Fig. 1(a) the radial permittivity of the electrolytic solutions confined into a spherical silica cavity. $\epsilon(r)$ can be expressed as $\epsilon(r) = 1 + \beta\epsilon_0^{-1}[\langle\mathbf{m}(r)\mathbf{M}\rangle_0 - \langle\mathbf{m}(r)\rangle_0\langle\mathbf{M}\rangle_0]$ [3,4]. Figure 1(a) shows an increase in ϵ_{cs} from $c = 0$ mol L^{-1} to 0.68 mol L^{-1} and a decrease to

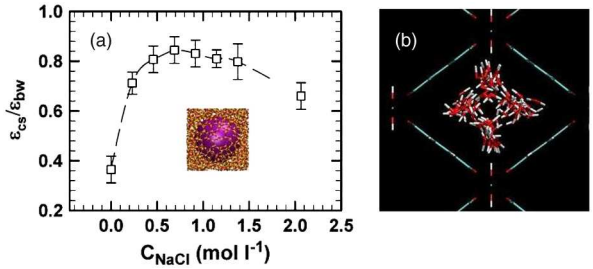

FIG. 1 (color online). (a) Ratio of the dielectric constant of NaCl solutions in a confined phase of various concentrations (ϵ_{cs}) to the dielectric constant of water in the bulk phase (ϵ^{bw}). (b) Illustration of confined water into the MIL-53(Cr) MOFs-type material.

2.0 mol L^{-1}. Figure 1(a) highlights an anomalous increase in the dielectric constant of confined NaCl solutions with the increase in salt concentration until a critical concentration. This result shows that our central result in Ref. [2] is well recovered from another confined geometry. To highlight the advantage to consider the Cartesian components of the dielectric tensor, we carried out MD simulations of water confined into a diamond-pore MIL-53 (Cr) metal-organics frameworks (MOFs) [5] [Fig. 1(b)]. By averaging the local components along to the r direction, we obtained $\epsilon_{xx} = 3.0 \pm 0.1$, $\epsilon_{yy} = 3.0 \pm 0.1$, and $\epsilon_{zz} = 28.0 \pm 1.0$. As in cylindrical confinement, a dielectric anisotropy of confined water was found. This result is in very good agreement with recent experiments [6,7].

To sump up, with cylindrical, spherical, and diamond pores, we recovered a dielectric anisotropy and an anomalous dielectric behavior in the presence of electrolytic solutions. This bears out the theoretical framework presented in Ref. [2].

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